

## Plasma catalysis in liquid water for CO<sub>2</sub> conversion

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Reacting CO<sub>2</sub> with water using plasma can be a reliable, cost-effective and environmentally friendly way to recycle this greenhouse gas, especially if the products are liquids since these are easier to store and transport. However, when this reaction is performed in gas-phase plasma, it doesn't usually lead to significant liquid production, producing mostly CO + H<sub>2</sub>. On the other hand, by using liquid water, even in the absence of catalysts, the reaction of CO<sub>2</sub> + H<sub>2</sub>O is able to produce longer molecules, mainly organic acids. Based on the prospect of producing higher oxygenates, we studied the effect of suspended MnO and Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> catalysts in liquid water while bubbling CO<sub>2</sub> plasma.

The plasma-catalytic experiments associated to the measurement of the Total Organic Carbon (TOC) showed, indeed, an effective conversion of CO<sub>2</sub> into liquid organic phases like Tridecanoic Acid. Furthermore, conversion is higher in the presence of catalysts and the highest activity is the obtained with Mn<sub>2</sub>O<sub>3</sub>, followed by Mn<sub>3</sub>O<sub>4</sub> and MnO, this is related with the energy necessary to subtract lattice oxygen, creating oxygen vacancies that are crucial for the catalytic process. To assess the change in the selectivity, organic phases were separated by evaporation of the solvent and analyzed by Fourier Transform Infrared spectroscopy. Those spectra showed the presence of linear monomer-like compounds and organic acids in the presence of catalysts. Accordingly, the presence of the solid catalysts changes the selectivity of the reaction to compounds with more C=O and C-O bonds.

The absence of C=O or C-O bonds in the case where no solids were used is evidence that oxygen is more importantly obtained from mechanisms involving the lattice oxygen in the metal oxides present. We then propose that the complete CO<sub>2</sub> breakage leads to the creation of \*HC radicals that can react with \*OH, ultimately chaining to (-CH<sub>2</sub>-)X as a result from the unique plasma-liquid interface. This mechanism is responsible for creating monomer-like linear molecules which grow by a process similar to radical polymerization, with the successive addition of radical blocks.

The same process occurs when solid particles are present but, in that case, there is the participation of CO<sub>2</sub> adsorbed species on the surface of the solids. The oxygen donated by the oxide increases the amount of carbon-oxygen bonds in the final product, explaining the difference in the products. Finally, it is possible to conclude that performing CO<sub>2</sub> conversion using liquid water as the hydrogen source is a promising technique to produce organic liquids especially with the addition of manganese oxides. Using two different catalysts it was possible to correlate the results with the lattice oxygen mobility and

conversion was increased up to 75%, while also changing the selectivity towards the production of organic acids.